

The Square-Shoulder-Asakura-Oosawa model

Riccardo Fantoni^{1,*}

¹ *Università di Trieste, Dipartimento di Fisica, strada Costiera 11, 34151 Grignano (Trieste), Italy*
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A new model for a colloidal size-asymmetric binary mixture is proposed: The Square-Shoulder-Asakura-Oosawa. This belongs to the larger class of non-additive hard-spheres models and has the property that its effective pair formulation is exact whenever the solvent particle fits inside the interstitial region of three touching solute particles. Therefore one can study its properties from the equivalent one-component effective problem. Some remarks on the phase diagram of this new model are also addressed.

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I. INTRODUCTION

Hard-sphere mixtures, additive or non-additive, sticky or not, etc., has very rich phase diagrams showing all three phases of matter: gas, liquid, and solid as well as mixed or demixed and percolating or glass. In some soft-matter laboratories [1–3], experimentalists are engineering always new kinds of (Boltzmann) particles and materials which sometimes show phase diagrams akin to the ones of hard-spheres. It is then very important to be able to predict with great accuracy the theoretical critical phenomena of hard-spheres. Whereas the properties of additive (sticky-)hard-spheres, non-additive (sticky-)hard-spheres has been carefully studied in the past. The same attention has not been given to non-additive square-shoulder-spheres. The one-component Square-Shoulder (SS) fluid model has been used for the first time by Hemmer and Stell [4, 5]. It may lead to an isostructural solid-solid transition [6], to a fluid-solid coexisting line with a maximum melting temperature [7], to unusual phase behaviors [8–10] as the reentrance of a hexatic phase in two dimensions [11, 12], and to a rich variety of (self-organized) ordered structures [13–16]. It has been used to describe the behavior of metallic glasses [7, 17], micellar [18] or granular [19] systems, colloidal suspensions [20, 21], primitive models of silica [22], aqueous solutions of electrolytes [23], and water [24, 25]. The SS model is the simplest of the class of core-softened potentials models for fluids [26] that can be used.

Recently it has been shown that augmenting the purely steric repulsion of the Asakura-Oosawa [27] model with a *soft* repulsion shell gives rise to temperature dependent interactions which in turn give rise to more realistic effective attractions for cosolute-macromolecule and specifically protective osmolytes systems [28, 29].

In the present work, following closely the theoretical framework of Ref. [36], we will study a highly size asymmetric binary mixture of Asakura-Oosawa where the un-

like species pair-interaction has a square-shoulder character.

II. DISCUSSION

An important problem in chemical physics is that of understanding how the behavior of the solute is influenced by the presence of the solvent. When there is a clear distinction between which are the solvent particles it is possible to describe the mixture as a binary one. Imagine for example that the solvent particles are the small “s” ones and the solute particles are the large “l” ones, then for a statistical physics description of the mixture we need to know the potential energy of interaction between the various particles, $U(\mathbf{r}_1^{(s)}, \mathbf{r}_2^{(s)}, \dots, \mathbf{r}_1^{(l)}, \mathbf{r}_2^{(l)}, \dots)$ where $\{\mathbf{r}_i^{(s)}\}$ are the coordinates of the small particles and $\{\mathbf{r}_i^{(l)}\}$ the ones of the large particles. It is always possible to write $U = U_{ss}(\mathbf{r}_1^{(s)}, \mathbf{r}_2^{(s)}, \dots) + U_{ll}(\mathbf{r}_1^{(l)}, \mathbf{r}_2^{(l)}, \dots) + U_{sl}(\mathbf{r}_1^{(s)}, \mathbf{r}_2^{(s)}, \dots, \mathbf{r}_1^{(l)}, \mathbf{r}_2^{(l)}, \dots)$, and, neglecting three bodies interactions (i.e. assuming the particles are non-deformable, non-polarizable, ...), we can say that U_{ss} contains all pair interactions between two small particles, U_{ll} contains all pair interactions between two large particles, and U_{sl} contains all pair interactions between a small and a large particle. Then, the influence of the solvent on the behavior of the solute has to be due to U_{sl} and U_{ss} . Clearly the problem simplifies when we can assume $U_{ss} = 0$ and under certain conditions [30] it can even be rewritten exactly in terms of an *effective* one-component one for only the large particle with a potential energy $U_{ll}^{\text{eff}}(\mathbf{r}_1^{(l)}, \mathbf{r}_2^{(l)}, \dots)$ with only pairwise interactions.

In a fluid binary mixture of small and large non overlapping hard bodies the small particles may induce a *depletion* entropic attraction between the big particles [27, 31, 32] when two of these are closer than the dimensions of the small bodies since in this case no small particle fit in the space between the two large particles but there will still be an osmotic pressure due to the small particles surrounding the two big particles pushing them

* rfantoni@ts.infn.it

together.

This depletion force serves an important stabilizing role in many biological and technological processes. Specifically, many osmolytes and polymeric crowders that are excluded from protein surfaces stabilize the more compact folded state.[28, 29]

Following the framework of Ref. [36], in order to understand theoretically this phenomenon we will introduce the following model size-asymmetric binary mixtures: A non-additive hard-sphere binary mixture [33–36] with the solvent particles non interacting among themselves, $\sigma_{ss} = 0$, the solute particles interacting as hard-spheres of diameter $\sigma_{ll} = \sigma_l$, and a square-shoulder interaction between the solvent particles and the solute particles where $\sigma_s = q\sigma_l$ is the diameter of the small spheres as seen by the large ones. The square-shoulder interaction occurs in a spherical shell of diameter between $\sigma_{sl} = \sigma_l(1 + q)/2$ and $\sigma_{sl}(1 + \lambda_{sl})$, the small and large particle are otherwise interacting as hard-spheres at distances smaller than σ_{sl} . Our size parameter q here plays the role of the usual non-additivity parameter $\Delta = \sigma_{sl}/\sigma_{sl}^{\text{add}} - 1 = q$ with $\sigma_{sl}^{\text{add}} = (\sigma_{ss} + \sigma_{ll})/2$.

This model being non-additive (with positive non-additivity) does not admit an analytical solution for the Percus-Yevick (PY) closure of the Ornstein-Zernike equations but under certain geometrical condition it admits an exact effective pair formulation [36].

We called this model the Square-Shoulder-Asakura-Oosawa (SSAO) model [27, 31, 32]. Of course, the more general formulation of the model is when one has σ_{ss}/σ_s different from 0, but in this more complicated case of an interacting solvent we would not be able to solve exactly analytically for the effective one-component problem [36].

Usually when talking about the AO model one refers to a colloid-polymer mixture where the depletant are linear homopolymers in a good solvent of radius of gyration $\sigma_s/2$, which, after tracing out the monomers degrees of freedom and replacing each chain with a particle coinciding with its center of mass [37], can be considered, for $\eta_s \lesssim 1$, to a first level of approximation, as non interacting among themselves but unable to penetrate a sphere of diameter $\sigma_s + \sigma_l$ around each colloidal particles. The colloidal particles are treated as hard spheres of diameter σ_l . In this work we will rather talk always about a solvent-solute mixture.

It is interesting to observe that when the temperature is set to infinity the SSAO model reduces to the usual AO one with a depletion range between σ_l and $2\sigma_{sl}$, whereas when it is set to zero it reduces to an AO model with a larger depletion range extending from σ_l to $2\sigma_{sl}(1 + \lambda_{sl})$.

To the best of our knowledge no numerical experiment has ever been tried on the full SSAO binary mixture.

We will now first discuss the derivation of the effective one-component problem of the SSAO model.

III. THE SSAO MODEL

Our SSAO binary mixture model is defined as follows

$$U_{ss} = \sum_{i < j} \varphi_{ss}(|\mathbf{r}_i^{(s)} - \mathbf{r}_j^{(s)}|), \quad (3.1)$$

$$U_{ll} = \sum_{i < j} \varphi_{ll}(|\mathbf{r}_i^{(l)} - \mathbf{r}_j^{(l)}|), \quad (3.2)$$

$$U_{sl} = \sum_{i,j} \varphi_{sl}(|\mathbf{r}_i^{(s)} - \mathbf{r}_j^{(l)}|), \quad (3.3)$$

$$f_{ss}(r) = e^{-\beta\varphi_{ss}(r)} - 1 = 0, \quad (3.4)$$

$$f_{ll}(r) = e^{-\beta\varphi_{ll}(r)} - 1 = -\theta(\sigma_{ll} - r), \quad (3.5)$$

$$f_{sl}(r) = e^{-\beta\varphi_{sl}(r)} - 1 = -\theta(\sigma_{sl} - r) + f_0(r), \quad (3.6)$$

where $\beta = 1/k_B T$ with T the absolute temperature, $\varphi_{ss}, \varphi_{ll}, \varphi_{sl}$ are the bare solvent-solvent, solute-solute, and solvent-solute pair-potentials respectively, f_{ss}, f_{ll}, f_{sl} the corresponding Mayer functions, $\sigma_{sl} = \sigma_l(1 + q)/2$, θ is the Heaviside step function, and the square-shoulder is

$$f_0(r) = \begin{cases} 0 & r < \sigma_{sl} \\ e^{-\beta\epsilon_{sl}} - 1 & \sigma_{sl} < r < \sigma_{sl}(1 + \lambda_{sl}) \\ 0 & r > \sigma_{sl}(1 + \lambda_{sl}) \end{cases}, \quad (3.7)$$

where $\epsilon_{sl} > 0$ is a positive constant. We can then introduce a reduced temperature as $T^* = 1/\beta\epsilon_{sl}$.

Model SSAO does not admit a PY analytic solution but admits an exact effective one-component description for $q < q_0 = 2/\sqrt{3} - 1 = 0.15470\dots$, when a solvent can fit into the inner volume created by three solutes at contact (or $q < 1$ in one spatial dimension [38]), so that a solvent particle cannot overlap simultaneously with more than two (nonoverlapping) solutes at contact. Following the derivation of Dijkstra et al. [30], we describe the mixture in a mixed canonical (for the solutes) and grand canonical (for the solvent) ensemble, which they call semi-grand-canonical (z_s, N_l, V, T) ensemble. It is then easy to show [36] that in this case, after integrating out the degrees of freedom of the solvent, the effective potential $\beta v_{ll}(r)$ is

$$\beta v_{ll}(r) = \beta\varphi_{ll}(r) - z_s \int d\mathbf{r}_s f_{sl}(r_s) f_{sl}(|\mathbf{r}_s - \mathbf{r}|), \quad (3.8)$$

which upon using Eq. (3.6) gives

$$\beta v_{ll}(r) = \begin{cases} +\infty & r < \sigma_l \\ v_0(r) & \sigma_l < r < 2\sigma_{sl}(1 + \lambda_{sl}) \\ 0 & r > 2\sigma_{sl}(1 + \lambda_{sl}) \end{cases}. \quad (3.9)$$

with

$$\begin{aligned}
& -v_0(r)/z_s = \\
& 2\mathcal{C}(r/2, \sigma_{sl}) - \\
& 2(e^{-\beta\epsilon_{sl}} - 1) [\mathcal{C}(r_<, \sigma_{sl}) + \mathcal{C}(r_>, \sigma_{sl}(1 + \lambda_{sl})) - 2\mathcal{C}(r/2, \sigma_{sl})] + \\
& 2(e^{-\beta\epsilon_{sl}} - 1)^2 \{\mathcal{C}(r/2, \sigma_{sl}(1 + \lambda_{sl})) - [\mathcal{C}(r_<, \sigma_{sl}) + \mathcal{C}(r_>, \sigma_{sl}(1 + \lambda_{sl})) - \mathcal{C}(r/2, \sigma_{sl})]\}, \tag{3.10}
\end{aligned}$$

where we denoted with $\mathcal{C}(R, \sigma)$ the volume of a spherical cap of height $\sigma - R$ in a sphere of radius σ , i.e.

$$\mathcal{C}(R, \sigma) = \frac{2\pi\sigma^3}{3} \left[1 - \frac{3R}{2\sigma} + \frac{1}{2} \left(\frac{R}{\sigma} \right)^3 \right] \theta(\sigma - R), \tag{3.11}$$

and $r_< + r_> = r$ with

$$r_< = \frac{r^2 + \sigma_{sl}^2 - \sigma_{sl}^2(1 + \lambda_{sl})^2}{2r}, \tag{3.12}$$

$$r_> = \frac{r^2 + \sigma_{sl}^2(1 + \lambda_{sl})^2 - \sigma_{sl}^2}{2r}. \tag{3.13}$$

In this case, from Dijkstra et al. [30] derivation, one finds that the exact cancellation of all Meyer diagrams higher than the two body one, occurs when [36]

$$\begin{aligned}
\frac{\sigma_{sl}(1 + \lambda_{sl}) - \sigma_l/2}{\sigma_l/2} &= q + \lambda_{sl} + q\lambda_{sl} < q_0 \\
&= \frac{2}{\sqrt{3}} - 1. \tag{3.14}
\end{aligned}$$

It is easy to show [36] that in the range $\sigma_l < r < 2\sigma_{sl}(1 + \lambda_{sl})$ one finds the result of Eq. (3.9) for the effective potential.

This is formally the same effective potential found in model SWAO of Ref. [36] where we change $\epsilon_{sl} \rightarrow -\epsilon_{sl}$. In the present case the sticky limit procedure would give the same AO model.

In Fig. 1 we show the effective potential for the SSAO binary mixture at various temperatures. From the figure

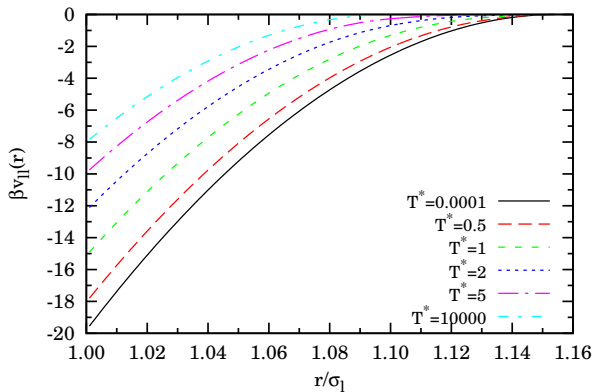


FIG. 1. (Color online) Effective potential for the SSAO mixture at various reduced temperatures and $q = 0.1, \lambda_{sl} = (q_0 - q)/(1 + q), \eta_s^{(r)} = 1/2$.

we see how at infinite temperature the SSAO reduces to

the usual AO model with a range $2\sigma_{sl}$ whereas at zero temperature it reduces to an AO model with a wider range extending to $2\sigma_{sl}(1 + \lambda_{sl})$. At intermediate temperatures the effective potential lies continuously between the two extreme cases. Thus, the soft shoulder repulsion enhances the depletion mechanism and the solute stabilization.

Here z_s is the solvent fugacity. We can introduce a solvent reservoir packing fraction $\eta_s^{(r)} = \pi z_s \sigma_s^3 / 6 = \eta_s e^{\beta \mu_s^{\text{ex}}}$, with μ_s^{ex} the excess (over the ideal gas) solvent chemical potential. The solvent reservoir is at the same temperature of the solute. $\eta_s^{(r)}$ is the packing fraction of the reservoir made of noninteracting solvent particles. The relationship between $\eta_s^{(r)}$ and η_s can be found calculating the average number of small solvent particles (see appendix C in Ref. [36]). Up to second order in η_l one finds

$$\begin{aligned}
\eta_s &\approx \eta_s^{(r)} \left[1 + \eta_l(1 + q)^3 (\lambda_{sl}(3 + \lambda_{sl}(3 + \lambda_{sl}))) e^{-\frac{1}{T^*}} \right. \\
&\quad \left. - (1 + \lambda_{sl})^3 - \frac{12\eta_l^2 q^3}{\sigma_l^3} \times \right. \\
&\quad \left. \int_{\sigma_l}^{\sigma_l(1+q)(1+\lambda_{sl})} dr r^2 (v_0/\eta_s^{(r)}) e^{-v_0(r)} \right]. \tag{3.15}
\end{aligned}$$

IV. THE NORO AND FRENKEL CRITERION

Noro and Frenkel [39] argued that the reduced second virial coefficient B_2/B_2^{HS} , rather than the range and the strength of the attractive interactions, could be the most convenient quantity to estimate the location of the gas-liquid critical point for many different colloidal suspensions. Their criticality criterion for particles with variable range attractions, complemented by the simulation value of the critical temperature obtained in Ref. [40] for the SHS model, yields $B_2/B_2^{\text{HS}} \approx -1.21$.

Applying Noro and Frenkel criticality criterion for particles with variable range attractions [39], complemented by the simulation value of the critical temperature obtained in Ref. [40] for the Sticky-Hard-Sphere model, to our effective one-component problem, we are led to conclude that criticality requires $B_2^{\text{eff}}/B_2^{\text{HS}} = -1.21$ where B_2^{eff} is the second virial coefficient of our effective solute-solute problem

$$B_2^{\text{eff}} = \frac{2\pi}{3} \left\{ \sigma_l^3 - 3 \int_{\sigma_l}^{\infty} dr r^2 \left[e^{-\beta v_{ll}(r)} - 1 \right] \right\}, \quad (4.1)$$

and $B_2^{\text{HS}} = 2\pi\sigma_l^3/3$ is the virial coefficient for HS of diameter σ_l . Note that B_2^{eff} can only be calculated numerically.

In Fig. 2 we show the coexistence curves for the phase diagram stemming from the Noro-Frenkel empirical criterion in the $(T^*, \eta_s^{(r)})$ plane, for the SSAO model with $q = 0.1$ for four values of $\lambda_{sl} = 0.001, 0.01, (q_0 - q)/(1 + q), 0.1$. For the last $\lambda_{sl} = 0.1$ case the effective potential of Eq. (3.9) is only an approximation. From the figure we see

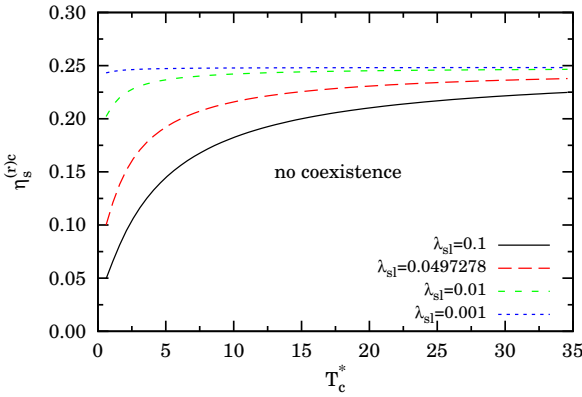


FIG. 2. (Color online) Phase diagram stemming from the Noro and Frenkel empirical criterion in the $(T^*, \eta_s^{(r)})$ plane, for a highly asymmetric, $q = 0.1$, SSAO for four values of λ_{sl} .

how even a small shoulder produces dramatic effects in the phase diagram, widening the fluid-fluid coexistence region.

V. PERTURBATION THEORY FOR THE SSAO MODEL

From the previous section we understood that the *hidden* or metastable fluid-fluid phase separation observed by Dijkstra et al. [30] in their study of the AO model could be enlarged by adding a soft unlike repulsion as in our SSAO model. Now we want to quantify this more precisely through first order perturbation theory [41]. Taking the HS as reference system we can write the

Helmholtz free energy per particle, $a = A/N$, as follows

$$\beta a_{ll} = \beta a_{\text{HS}} + 12\eta_l \int_{\sigma_l}^{\sigma_l(1+q)(1+\lambda_{sl})} \beta v_{ll}(r) g_{\text{HS}}(r) r^2 dr, \quad (5.1)$$

where $\beta a_{\text{HS}} = (4\eta_l - 3\eta_l^2)/(1 - \eta_l)^2 + \ln(\eta_l) + \text{constants}$ is the Carnahan-Starling [42] expression for HS, βv_{ll} the effective pair-potential of the SSAO model of Eq. (3.9), and g_{HS} is the HS radial distribution function in the PY approximation [43], which in the interval $1 < r < (1 + q)(1 + \lambda_{sl}) < 2$ can be written as follows

$$r g_{\text{HS}}(r) = \sum_{i=0}^2 \lim_{t \rightarrow t_i} (t - t_i) t \frac{L(t)}{S(t)} e^{t(r-1)}, \quad (5.2)$$

where we are measuring lengths in units of σ_l ,

$$S(t) = (1 - \eta_l)^2 t^3 + 6\eta_l(1 - \eta_l)t^2 + 18\eta_l^2 t - 12\eta_l(1 + 2\eta_l), \quad (5.3)$$

$$L(t) = (1 + \eta_l/2)t + 1 + 2\eta_l, \quad (5.4)$$

and $t_i (i = 0, 1, 2)$ are the zeros of $S(t)$. The first order Helmholtz free energy of Eq. (5.1) can thus be calculated analytically.

The compressibility factor $Z = \beta p/\rho$ and chemical potential μ are then found through

$$Z_l = \eta_l \left. \frac{\partial \beta a_{ll}}{\partial \eta_l} \right|_{\eta_s^{(r)}}, \quad (5.5)$$

$$\beta \mu_l = Z_l + \beta a_{ll}. \quad (5.6)$$

The critical point $(\eta_s^{(r)c}, \eta_l^c)$ is determined by numerically solving the following system of equations

$$\left. \frac{\partial Z_l \eta_l}{\partial \eta_l} \right|_{\eta_s^{(r)c}, \eta_l^c} = 0, \quad (5.7)$$

$$\left. \frac{\partial^2 Z_l \eta_l}{\partial \eta_l^2} \right|_{\eta_s^{(r)c}, \eta_l^c} = 0. \quad (5.8)$$

In Fig. 3 we show the critical point $(\eta_s^{(r)c}, \eta_l^c)$ for the fluid-fluid coexistence of the SSAO model for $q = 0.1$ and $\lambda_{sl} = 0.001$, near to the AO, and $\lambda_{sl} = (q_0 - q)/(1 + q)$, the full SSAO, as a function of the reduced temperature, T^* . The figure confirms the scenario predicted in the previous section from the Noro-Frenkel criterion but gives additional information on the critical solvent and solute packing fractions, η_s^c and η_l^c respectively. Of course we expect a breakdown of the perturbation theory treatment as soon as the depletion mechanism becomes too strong. Also as soon as $q > q_0$ we are neglecting three-body (and higher) terms.

VI. CONCLUSIONS

We studied a new colloidal strongly asymmetric binary mixture of (small) solvent and (large) solute particles, where unlike particles interact through the repulsive Square-Shoulder (SS) pair-potential, that we called

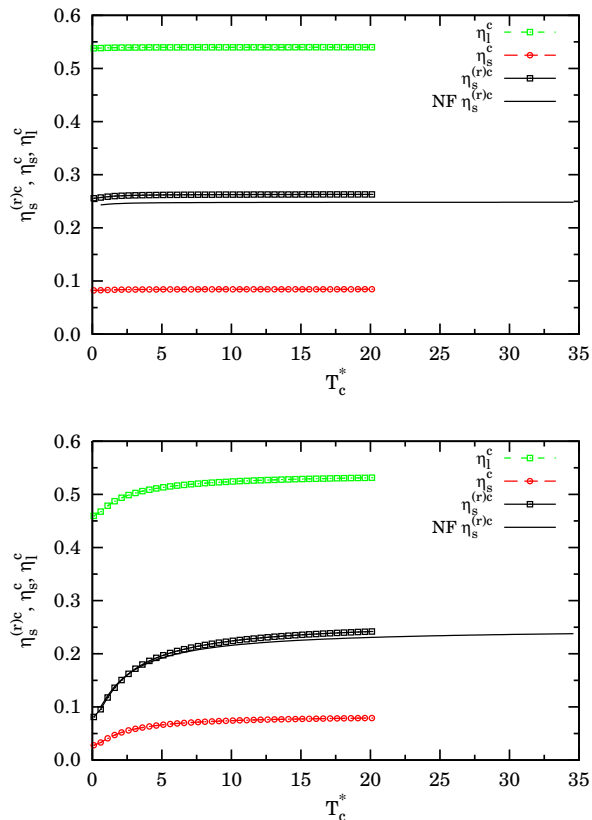


FIG. 3. (Color online) Critical point for the fluid-fluid coexistence in SSAO for $q = 0.1$ and $\lambda_{sl} = 0.001$ (top panel) and $\lambda_{sl} = (q_0 - q)/(1 + q)$ (bottom panel) as a function of T_c^* . The lines with symbols are obtained from thermodynamic perturbation theory, whereas the solid line corresponds to the Noro and Frenkel criterion of Fig. 2. Eq. (3.15) is used for the conversion between the reservoir density and the solvent density.

the Square-Shoulder-Asakura-Oosawa (SSAO) model. Whenever the solvent particle fits inside the interstitial region of three touching solute particles we were able to derive exactly analytically an effective solute-solute pair-potential and discussed the corresponding phase behaviors, as obtained from the resulting effective one-component system.

We found that the mere presence of the soft repulsion in the spherical shell of the SS unlike pair-interaction augments the depletion mechanism typical of the underlying Asakura-Oosawa (AO) mixture. Applying the Noro and Frenkel criterion we saw that this, in turn, enlarges (and may stabilize) the metastable fluid-fluid phase coexistence region typical of the strongly asymmetric AO model at large reservoir packing fractions. A first order thermodynamic perturbation theory nicely confirms the scenario depicted by such criterion.

This phenomenon can be relevant in the experimental study of colloidal suspensions undergoing a fluid-fluid phase transition in the laboratory. Whenever the mathematical mixture just described represents a good model for a real mixture it should be expected that the main effect of the presence of the additional repulsive shell in the unlike species pair-interaction is to increase the depletion mechanism and in turn to enlarge the phase coexistence region of the phase diagram.

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